(54) Titre : PROCEDE DE RECUPERATION DE METAUX PRECIEUX RESIDUELS DANS DES SCORIES DE FONDERIE ET DE CONVERTISSEUR
(54) Title: PROCESS FOR THE RECOVERY OF RESIDUAL METAL VALUES FROM SMELTER WASTE SLAGS, AND FROM CONVERTER SLAGS

NICKEL-COPPER-COBALT SULPHIDE
FEEDS AND FLUXES

PRIMARY SMELTING FURNACE

NICKEL-COPPER-COBALT
FURNACE MATTE

WASTE/DUMP SLAG   CONVERTER SLAG

CONVERTING

NICKEL-COPPER-COBALT
BESSEMER MATTE

COOLING/CRYSTALLIZATION

CRUSHING & GRINDING

WATER → PULPING

BY-PRODUCT → PRESSURE LEACHING ← OXYGEN
SULPHURIC
ACID

WATER
FLOCCULANT → COUNTER-CURRENT-DECANTATION ----→ TO TAILINGS PLACEMENT

NEUTRALIZING & → METALS RECOVERY ----→ TO WASTE WATER
PRECIPITATION   TREATMENT
AGENTS   & DISPOSAL

INTERMEDIATE
NICKEL-COPPER-COBALT PRODUCTS

LEGEND
Solids ——→
Pulps ----→
Liquids ····→
Gases ——→

(57) Abrégé/Abstract:
This invention provides a process for economical extraction of residual base metal values in furnace slags, by utilizing smelter by-product sulphuric acid for the pressure leaching of such slags after sufficient initial slow-solidification to induce crystallization.

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(57) Abrégé(suite)/Abstract(continued):
After final solidification and cooling the slags are ground and pulped, mixed with sulphuric acid in an autoclave, and reacted at temperatures up to 275°C and pressures up to about 940psi when applying an oxygen over-pressure of up to 75psi, for up to 2 hours. High degrees of extraction of contained nickel, copper, cobalt and zinc if present, are achieved which are subsequently recovered from the leachate. Whereas the furnace slags, as produced and untreated, present a potential long term environmental hazard, after extraction of their base metal values they are rendered virtually benign vis-à-vis the environment. This method of pressure leaching can be applied to crystallized converter slags enriched in cobalt during the smelting of metal and copper sulphide ores.

ABSTRACT

This invention provides a process for economical extraction of residual base metal values in furnace slags, by utilizing smelter by-product sulphuric acid for the pressure leaching of such slags after sufficient initial slow-solidification to induce crystallization. After final solidification and cooling the slags are ground and pulped, mixed with sulphuric acid in an autoclave, and reacted at temperatures up to 275°C and pressures up to about 940psi when applying an oxygen over-pressure of up to 75psi, for up to 2 hours. High degrees of extraction of contained nickel, copper, cobalt and zinc if present, are achieved which are subsequently recovered from the leachate. Whereas the furnace slags, as produced and untreated, present a potential long term environmental hazard, after extraction of their base metal values they are rendered virtually benign vis-à-vis the environment. This method of pressure leaching can be applied to crystallized converter slags enriched in cobalt during the smelting of metal and copper sulphide ores.

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PROCESS FOR THE RECOVERY OF RESIDUAL METAL VALUES FROM SMELTER WASTE SLAGS, AND FROM CONVERTER SLAGS

FIELD OF THE INVENTION

5   The present invention relates to a process for the recovery of residual

metal values from smelter waste slags and from converter slags.

BACKGROUND OF THE INVENTION

In non-ferrous smelting operations, such as in the smelting of nickel

10   sulphide ores and/or concentrates, copper sulphide ores and/or concentrates,

and nickel-copper sulphide ores and/or concentrates, the nickel and copper are

first recovered in an upgraded intermediate sulphide product usually referred to

as "furnace matte", while the iron sulphide component of the feed materials is

oxidized to SO_2 gas and iron oxide which is fluxed with silica and combined with

15   the other oxidic rock minerals that arrived with the ore and/or concentrates to

produce a "slag" waste product. This slag is usually of comparable tonnage to

the tonnage of the feed ore and/or concentrate. This slag is transported either in

the molten state by slag trains or specialized truck carriers to slag dumps or as a

granulated solid pumped to de-watering dumps. These dump slags can contain

20   3% to 8% of the nickel and copper values in the original ore and/or concentrate

feed, reflecting overall smelter recoveries of 97% to 92% of these metals.

All nickel sulphide ores invariably contain minor amounts of cobalt as well

as of copper. The cobalt content usually falls between 2% and 4% that of the

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nickel content, while the copper can be 5% of the nickel or higher. Because of it's propensity to oxidize in preference to the nickel, cobalt recovery into the matte could vary between about 25% and 50%, with the remainder reporting to the slag, largely in oxide form. The nickel lost to the waste slag reports both in sulphide and oxide forms, while the copper lost to the waste slag reports largely in sulphide form.

In the case of copper sulphide ores and/or concentrates that may contain minor amounts of nickel and/or cobalt a large proportion of the nickel and/or cobalt is generally lost as oxides incorporated in the silicate waste slag. And, in the case of copper sulphide concentrates containing significant amounts of zinc, the zinc reports as oxide fume in the smelter off-gases and as oxide incorporated in the silicate waste slag.

Large stores of dump slags are prominent symbols of existing and past smelting operations. While they appear to be innocuous, being hard solid materials, they are problematic as they do not support plant growth. To effect any sort of vegetation of such dumps requires importation of soil to provide a cover and a base for plant seeding and growth. Left uncovered and unprotected, these dump slags are leached by the rains, albeit very slowly, releasing, nickel, copper, cobalt and zinc if present, to the external environment in minute quantities, but at concentrations that could exceed regulation levels for discharge waters.

The large dumps of waste slags have received considerable attention by researchers interested in recovering their residual metal values, particularly the

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residual nickel and cobalt. Being that the nickel and cobalt in the slags exist as oxides chemically bound with silica to form a fayalite mineral, their recovery by conventional smelting technology is very costly. The slags would first need to be re-melted, the nickel and cobalt reduced and sulphided along with any copper that may be present, to be collected and concentrated in an intermediate matte product. This primary matte may, or may not, be upgraded by oxidation and removal of some of the contained iron sulphide, before being cast and cooled and prepared for hydrometallurgical processing. The hydrometallurgical treatment could begin with pressure leaching to solubilize all of the base metals in preparation for separation, refining and conversion into saleable products. While technically feasible, the outstanding problem with this treatment/recovery process is one of economics. Quite evidently, no one to date has come up with an economically viable process for re-treatment of the waste dump slags generated by nickel-copper smelters, since such slags remain dormant at shutdown operations and continue to grow at on-going operations. It should be recognized that some of these slags have been used for constructing highway and railroad beds and for mine backfill.

Smelter slags can be the waste products of various types of smelting operations (See Figure 1). Historically, starting with the latter part of the 19th century, coarse/lumpy copper sulphide ores and nickel-copper sulphide ores were smelted directly in blast furnaces fuelled with coarse coke, to produce furnace matte containing 95% or more of the nickel and copper and a lesser proportion of any cobalt accompanying the nickel, as well as a large quantity of

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iron sulphide. Also, a significant quantity of slag was produced in the blast furnace itself, from the oxide minerals that arrived in the ores. The molten furnace matte tapped from the blast furnace settler would be transferred to Pierce Smith converters for removal of the iron sulphide by oxidizing its sulphur to SO_2 and its iron to iron oxide which would be fluxed by the addition of quartz or silica sand to produce a silicate/fayalite slag which was returned to the blast furnace settler. The blend of slag produced directly in the blast furnace itself and the slag produced in the converters and returned to the blast furnace settler were skimmed into slag pots and transported to slag dumps by slag trains, or were granulated in water and pumped to disposal areas.

With the advent of chemical flotation technology, the coarse ores were further broken down and ground into fine particles to permit separation of the sulphide minerals into a concentrate fraction with elevated contents of nickel, copper and cobalt. The other fraction composed principally of the oxidic rock minerals and low in residual metal values would comprise the tailings, for permanent disposal to tailings settling and de-watering areas. To prepare such finely ground concentrates for feeding to the blast furnaces they were sintered on traveling grate machines into large lumpy form to be charged along with the direct smelting lumpy ores. Thus, the blast furnaces supported by sintering machines were able to accommodate and take advantage of the new flotation technology. By processing the higher-grade concentrates the blast furnaces were able to raise their productivity and remain viable and competitive well into the 20th century. However, the advent of the reverberatory furnace firstly and the

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electric furnace secondly, gradually displaced the blast furnace. Vestiges of the blast furnace operations are the large stocks of waste dump slags hosting low contents but large quantities of nickel, copper and cobalt.

5   The use of reverberatory furnaces, introduced in the 1920's for nickel and copper smelting, expanded rapidly as they were designed to smelt the concentrates without sintering, either directly or after drying and partial roasting/oxidation in Herreschoff roasters. The reverberatory furnace fired with coal or natural gas soon had a competitor, the electric furnace. In both cases the iron sulphide would be oxidized to SO_2 and iron oxide, and the iron oxide would

10   be fluxed with silica to produce a silicate/fayalite slag, and the slags leaving the reverberatory and/or electric furnaces would be transported to waste dumps either in the molten state or pumped with water in granulated form. As is the case of the blast furnaces, these dump slags contain residual nickel, copper and cobalt values.

15   In the case of smelting copper concentrates obtained by chemical flotation and separation of copper-zinc sulphide ores, such copper concentrates would contain significant quantities of zinc, and such zinc would report largely as an oxide in the furnace slag. Some of these slags have been sufficiently high in zinc content to warrant slag-cleaning treatment by injection of fine coal in a slag-

20   fuming furnace. The zinc oxide would be reduced and the zinc metal would be vaporized and subsequently re-oxidized; and the zinc oxide fume would exit with the slag-fuming furnace off-gases from which the zinc oxide would be recovered.

Around 1950, the first use of bulk commercial grade oxygen for direct, autogenous smelting of copper concentrates was demonstrated. The new smelting technique is known as Oxygen Flash Smelting. It does not require any extraneous fuel as the heat required for smelting is generated by the oxidation of about half of the iron sulphide which is the main sulphide component of the copper, nickel and/or nickel-copper concentrates. The iron sulphide is oxidized to a strong SO_2 gas and iron oxide which is fluxed with silica into a silicate/fayalite slag. The rich SO_2 gas can proceed to liquifaction for sale as liquid SO_2, or it may be converted into sulphuric acid. The flash furnace matte normally proceeds to Pierce Smith converters for oxidation of the remainder of the iron sulphide, with the converter slag returning to the flash furnace. The blended slag then goes to waste dump disposal. Because of low energy consumption, strong valuable SO_2 gas production and high productivity, the oxygen flash furnace has come into prominence as the preferred smelting technology for copper concentrates, and more recently for nickel and nickel-copper concentrates as well. In all cases, the flash furnace slags proceed to waste dumps either directly or after a degree of reduction to lower the residual nickel,copper and cobalt contents.

While other smelting technologies have been developed and proposed, the bulk of non-ferrous smelting is carried out in oxygen flash furnaces or electric furnaces, with several reverberatory furnace installations still active and with blast furnaces essentially completely displaced. A continuous copper smelting

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process has been recently developed by Mitsubishi Industries, which starts with a version of up-front oxygen smelting.

By re-processing the old waste dump slags and the slags currently being produced and going to waste dumps, an ecological improvement is brought about. By extracting the residual base metal contents, the resulting "cleaned" residues should not present any short term or any long-term threats to the environment, as very little nickel, copper, cobalt or zinc would remain.

Figure 1, summarizes the main features of the various conventional nickel-copper smelting technologies. It will be known to the smelter practitioner and informed observer, that one principal function of the non-ferrous smelter is to oxidize the large proportion of iron sulphide present in all copper and nickel sulphide ores and concentrates, and to dispose of large quantities of SO_2 and iron oxide. The SO_2 gas is either liquefied to liquid SO_2 for market to the extent that such markets exist, with the remainder converted to sulphuric acid; while the iron oxide is fluxed with silica to a silicate/fayalite slag. There is a growing amount of smelter acid being produced that must be disposed of at the rate that it is being produced, since there is no economical way of storing it in such large quantities. Indeed, some smelters must pay to have their acid transported to distant markets.

A significant aspect in the smelting of nickel sulphide, copper sulphide and nickel-copper sulphide ores and concentrates, is that the cobalt builds up a circulating load between the primary melting stage and the converting stage. This aspect results in the high-iron converter slags that are routinely returned to

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the primary melting stage having a high cobalt content, i.e., with a cobalt to nickel ratio that could be 2 to 4 times that of the incoming ore and/or concentrate feeds. One way of improving overall cobalt recovery in such smelting operations would be to bleed off a portion of the converting slags containing the highest cobalt

5   values, and redirecting them to separate hydrometallurgical treatment for recovery of the cobalt as well as of the associated nickel and copper while rendering essentially all of the iron as a solid discard residue.

Subjecting slags from copper smelting operations, both dump slags and converter slags, to pressure leaching with sulphuric acid with an oxygen over-

10   pressure has been studied by earlier researchers. Klein et al. (Lawrence C. Klein and Laurence G. Stevens, "Recovery of Copper Values from Slags" U.S. Patent No. 3,632,308, Jan.4, 1972) disclose recovering "over 95% by weight of the copper" from finely ground granulated slag, and have demonstrated the criticality of applying an oxygen over-pressure. Those skilled in the art recognize that the

15   copper in furnace slags exists largely as a distinct finely-dispersed copper sulphide phase, and appreciate the importance of maintaining an oxygen over-pressure to oxidize and solubilize such copper sulphide and any other sulphides that might be present.

Anand et al. (K. Anand, K. Sarveswara Rao and P.K. Jena "Pressure

20   Leaching of Copper Converter Slag Using Dilute Sulphuric Acid for the Extraction of Cobalt, Nickel and Copper Values" Hydrometallurgy, 10 (1983), 315-312) describe pressure leaching conditions for extracting copper, nickel and cobalt from copper converter slags. They demonstrated that 92% of the copper and

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over 95% of the nickel and cobalt in the converter slags can be solubilized by leaching at relatively low pulp density of 10% solids, at H_2SO_4 concentrations of 1.75 times stoichiometric, with oxygen over-pressure of 0.5 MPa or higher, at 130°C and with a leaching time of 4 hours.

5   Linblad et al. (Kenneth D. Linblad and Ralph E. Dufresne, "Acid Leach of Copper Reverberatory Slag - A New Approach" Journal of Metals, February, 1974) carry out atmospheric leaching of copper reverberatory dump slag containing copper and zinc values, with sulphuric acid after extensive "aging" periods. In their examples they recover 85% of the copper, and 93% of the zinc

10   along with a very large proportion of the iron.

The two technical papers by Terry (B. Terry "The Acid Decomposition of Silicate Minerals, Part1: Reactivities and Modes of Dissolution of Silicates" Hydrometallurgy, 10 (1983), 135-150; and B. Terry "The Acid Decomposition of silicate Minerals, Part2: Hydrometallurgical Applications" Hydrometallurgy, 10

15   (1983), 151-171) while demonstrating that a wide variety of silicate minerals, including fayalite which is the main mineral component of base metal smelter slags, are soluble in sulphuric acid, does not teach how to obtain high extractions of base metals such as copper, nickel, cobalt and zinc from such silicate slags.

Sobol, (S.I. Sobol, "Chemistry and Kinetics of Oxidative Sulphuric Acid

20   Leaching of Cobalt-bearing Converter Slags" Proceedings of the Paul E. Queneau International Symposium Extractive Metallurgy of Copper, Nickel and Cobalt, Volume1, Fundamental Aspects, 1993) also tested pressure leaching of converter slags but at higher temperatures and pressures, and at higher pulp

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densities than Anand et al. Regarding the latter, he points out that "....conditions which the authors called optimal would require large amount of expensive equipment because of low parameters of the process and dilute pulps.....increase of the density of the latter reduces considerably the recovery of non-ferrous metals as well as the selectivity of separation thereof from iron and silica". Sobol, on the other hand, worked at 20% solids and higher, and at temperatures of 150°C and also at 190°C. He referred to, without demonstrating, tests "carried out at a temperature up to 205°C and liquid:solid ratio equal to 1 and indicated that reaching cobalt losses with dumpy tails on the level of 250g/t of iron is practicable". In his experimental data at 150°C and 190°C he showed extractions of 90+% of the nickel copper and cobalt in less than 60 minutes.

SUMMARY OF THE INVENTION

The present invention relates to a process for economically recovering the residual nickel, copper, cobalt and zinc values, from waste/ dump slags, from non-ferrous smelters. It is also applicable to the processing of converter slags, which are normally internally recycled in such smelters.

The present invention provides a process of extracting metal values from base metal metallurgical fayalite slags, comprising the steps of:

cooling molten iron silicate/fayalite slag at a sufficiently slow solidification rate for producing a substantially crystallized fayalite slag and to avoid obtaining a substantially amorphous fayalite slag;

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crushing and grinding said crystallized fayalite slag and pulping said

ground crystallized fayalite slag with water to produce a pulped slag;

adding an effective amount of sulphuric acid to the pulped slag to produce

a mixture of sulphuric acid and pulped slag, agitating said mixture at elevated

5　　temperatures above about 200°C and elevated pressures, under an over-

pressure of oxygen for an effective period of time whereby metal oxides are

leached from said pulped slag to produce a leach pulp;

separating the leach pulp into a leachate and leached tailings;

recovering metal values from said leachate.

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BRIEF DESCRIPTION OF THE DRAWINGS

The process for recovery of metal values from smelter slags in

accordance with the present invention will now be described, by way of example

only, reference being had to the accompanying drawings, in which:

15　　Figure 1 is a general flowsheet depiction of the two major prior art steps

common to conventional nickel-copper smelting;

Figure 2 outlines the principal processing steps for recovering the residual

nickel, copper and cobalt values from waste/dump furnace slags according to the

teachings of the present invention;

20　　Figure 3 is an alternative embodiment of the method shown if Figure 2;

Figure 4 is a variation of the present invention, as applied to converter

slags for the recovery of nickel, copper and cobalt;

Figure 5 is an alternative embodiment of the method shown if Figure 4;

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Figure 6 shows the x-ray diffraction (XRD) spectrum of two electric furnace feed slags with poor NiCo recovery; and

Figure 7 shows an XRD of two electric furnace feed slags with good NiCo recovery.

DETAILED DESCRIPTION OF THE INVENTION

The present invention is directed to a method for economically processing waste dump slags from base metals smelting units to recover their residual nickel, copper, cobalt and zinc values. This invention provides a method of converting a primary waste dump material that could present a long term threat to the environment into a secondary, virtually benign waste dump material, by the extraction of the residual nickel, copper, cobalt, and zinc from the primary waste dump material.

Figure 2 shows a flowsheet illustrating the steps of the present process. The first step comprises the furnace slag being cooled to induce crystallization in the molten slag. Upon solidification and crystallization, and after complete cooling, the slag is crushed, ground and pulped with water, in preparing it as feed to an autoclave; and oxygen gas is also introduced to maintain a suitable over-pressure of up to 75 psi, over and above the steam pressure that would relate to the reaction temperature maintained in the autoclave.

After providing for an appropriate time for leaching of up to two hours, the pulp discharging from the autoclave, after the pressure and temperature have been let down, passes to a counter-current-decantation (CCD) circuit for separation of leachate containing the metal values, and the leached tailings. The

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leachate is passed on to a metals recovery circuit while the leached solids go to tailings placement. Metal values can be recovered from the leachate by neutralization and precipitation by a variety of agents to yield intermediate products suitable as feeds for nickel-cobalt refineries.

5   Those skilled in the art will appreciate that the metal values can be recovered from the leachate, after partial neutralization to remove dissolved ferric iron, by other means such as by solvent extraction and/or ion exchange technologies. Also, those skilled in the art will recognize that in certain cases it could prove beneficial to effect the partial neutralization of the leach pulp

10   emanating from the autoclave to a pH of about 3.5 to about 4.5 to precipitate any ferric iron that would be present in solution, before passing on to the CCD circuit. Figure 3 shows this variation of the method of Figure in which prior to the step of separating the leach pulp into a leachate and leached tailings, limestone is mixed with the leach pulp. The stripped solution after metals recovery, passes on to

15   waste water treatment to insure that the base metal contents are below regulated limits, before being discharged to any natural water course.

The present invention may be applied to the treatment of converter slags in a similar manner as applied to waste dump slags.

A variation of the process is shown in Figure 4 where a major proportion of

20   the converter slag can be redirected to cooling and crystallization, after which the slag is subjected to the same preparatory steps, leaching conditions and metals recovery treatments applied to furnace waste/dump slags. In directing all or a portion of converter slag to such processing, the quantity of furnace waste/dump

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slag is substantially reduced, and its base metal contents are significantly lowered, thereby yielding overall beneficial results. A variation of the method of Figure 4 is illustrated in the flowsheet of Figure 5 in which prior to the step of separating the leach pulp into a leachate and leached tailings, limestone is mixed with the leach pulp similar to the discussion of the process of Figure 3.

The present invention also relates to the use of by-product smelter sulphuric acid for the leaching of smelter waste/dump slag for the recovery of the residual nickel, copper, cobalt and zinc values of such slags, to yield an overall economic benefit to the smelting operation.

The present invention focuses primarily on metallurgical waste/dump slags from non-ferrous smelting operations, and on the practicality of utilizing by-product sulphuric acid produced by such operations to effect the primary extractions of base metal values remaining in said slags. Concomitantly, the final residue after extraction of the base metals is virtually benign vis-à-vis the external environment. In essence, a waste product is converted into a valuable source of non-ferrous metals.

In defining optimal treatment/processing conditions, the inventors have discovered that the physical nature of the slag has profound effect on the amenability of the slag to render high degrees of extraction of the metal values contained by the slag.

The present invention discloses how initial slow-cooling of the molten non-ferrous slag to effect crystallization of fayalite, from normal smelting temperatures of around 1250°C to about 1000°C, renders the slag amenable to high degrees

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of extraction of the contained base metal values by subsequent leaching with sulphuric acid at elevated temperatures and pressures and under an oxygen over-pressure. The inventors have also demonstrated that smelter slags that have been rapidly cooled so as to yield an amorphous structure yield poor extractions under similar conditions of leaching.

It was also discovered that the initial cooling rates and overall degree of cooling undergone by molten non-ferrous smelter slags in slag ladles, as often employed in commercial practice, during the time of skimming of said slags into the ladles plus the time of the subsequent transport of said filled ladles to the slag dumps, with completion of solidification on said dumps, is adequate to effect the crystallization of fayalite essential for high base metal extractions upon subsequent pressure leaching with acid.

Those skilled in the art and familiar with smelting will appreciate that solidification of a slag starts at the "liquidus" temperature and is completed at the "solidus" temperature, and that these temperatures will vary somewhat depending on the composition of the slag. With iron silicate/fayalite slags, both in large scale practice and in laboratory experiments conducted in connection with the present invention, the liquidus normally falls under about 1200°C but above about 1100°C; and the solidus generally falls between about 1025°C and 1075°C, often around 1050°C. Furthermore, the expert will appreciate that a considerable amount of heat units is given off due to the heat of fusion of the slag; i.e., final solidification occurs over a significant period of time. When one relates this knowledge and experience to the commercial practice of employing

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initial slow cooling, a crystalline structure is induced which yields high extractions of the base metal values of, nickel, copper, cobalt and zinc when subjected to the same standard acid pressure leaching test conditions.

The present invention represents a major technological step forward in teaching how to economically recover base metal values from non-ferrous smelter slags that heretofore have been considered as worthless discard materials. The invention also teaches how to make effective use of another by-product of the sulphide smelting operations, namely the sulphuric acid which must be disposed of by finding an end use.

Primary metallurgical slags produced by the smelting of nickel-copper sulphide ores and concentrates, containing residual amounts of nickel,copper, cobalt and trace amounts of zinc are slowly-solidified from their normal smelting temperatures of between about 1200°C and 1300°C first in slag ladles to induce crystallization, before being cast onto slag dumps for completion of solidification and for final cooling. Tests FF-1, FF-2, FF-4, FF-5 and FF-6 of Example 2, test EFSb-D of Example 3, and tests BFSa-1, BFSa-2 and BFSb of Example 4 were carried out on samples taken from slags that were slowly solidified and crystallized on a commercial scale; while test EFSa G-SC of Example 3, were carried out on a slag that was slowly solidified and crystrallized in the laboratory. In these tests, the solidified and cooled slags are finely ground to essentially minus 100 mesh size, and are then pulped with a liquid, preferably water, to produce a pulped slag. The pulped slag is then subjected to digestion with sulphuric acid produced by such smelting operations, at elevated temperatures

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above about 200°C and up to 275°C with an oxygen over-pressure of up to 75

psi and at total pressures above about 300 psi and up to 940psi, to achieve high

degrees of extraction, of at least 90% of each of the nickel, copper and cobalt

values in the majority of cases, and whereby a secondary leached waste residue

5   is produced which is virtually benign vis-à-vis the external environment.

Nickel, copper and cobalt values are effectively and equally well extracted

from intermediate converter slags produced in the smelting of nickel and copper

sulphide concentrates. As described in Example 1, tests Csa-2 and CSb-1, the

slowly cooled and crystallized, finely-ground converter slags are pulped by being

10   mixed with water and then directly leached with sulphuric acid at an elevated

temperature of 250°C and total pressure of about 650psi when applying an

oxygen over-pressure of 75psi, with the sulphuric acid addition being in excess of

stoichiometric requirements after taking into account the acid generated by

oxidation of the sulphide sulphur contained in the slags. After 60 minutes of

15   leaching, extractions of nickel, copper and cobalt were above 90% in all cases.

Copper, zinc and any associated nickel and cobalt values are extracted

from metallurgical slags produced by the smelting of zinciferous copper sulphide

concentrates, as reflected in Example 5. Best extractions were achieved in test

MFSb-SC in which the crystallized, cooled slag was finely ground to largely pass

20   through a 100 mesh sieve and was then pulped with water. The pulped slag was

then leached with 40% by weight of sulphuric acid at a pulp density of about 27%

at an elevated temperature of 250°C and at an elevated pressure of about 650

psi when applying an oxygen over-pressure of 75psi. This resulted in high

degrees of extraction of the contained metal values copper, zinc and the associated nickel and cobalt, in a reaction time of two hours, being 90+% for copper, nickel and cobalt, and 80+% for zinc.

A preferred initial solidification rate to effect crystallization through the temperature range between about 1200°C and about 1025°C is between about 1°C/minute and about 10°C/minute. For example, the hot, molten iron silicate slag at a smelting temperature of about 1200°C to about 1300°C could be skimmed into large slag ladles containing about 10 to 20 tonnes of such molten slag, in which ladles the initial cooling begins by heat radiation from the ladles and in which further cooling continues during holding and transport to a slag dump, over a total time period of at least about 15 minutes and up to about 60 minutes, before being discharged onto the slag dump for completion of solidification and final cooling.

The pregnant solutions obtained after separating out the leached waste residues proceed to a two-stage treatment of partial neutralization with limestone to eliminate the bulk of the iron, and after solid-liquid separations the solutions are reacted with a sulphide compound to precipitate an intermediate sulphide product containing the bulk of the base metals that had been extracted from the waste smelter slags. As shown in Figures 3 and 5, the partial neutralization with limestone may be effected prior to the solid-liquid separation. Those skilled in the art of metals recovery and refining will be familiar with the possibility of recovering the nickel, copper and cobalt values from the partially neutralized, substantially iron-free, pregnant solutions by further neutralization with agents

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such as magnesia or soda ash to precipitate these metal values as intermediate hydroxide or carbonate products, which then proceed to nickel-cobalt refineries. Alternatively, solvent extraction or ion exchange technologies may be applied to the pregnant solutions to concentrate and separate the base metals into separate

5 concentrate streams followed by production of refined metals by electrowinning or other means.

The invention is illustrated in more detail in the following illustrative, non-limiting examples, already referred to above.

10 **EXAMPLES**

The various smelter slags received and tested are described in Table 1.

Table 1: Chemical Composition of the Smelter Slags as Received

Code	Name & Description	%Ni	%Co	%Cu	%Zn	%Fe	%SiO₂	%S
CSa	Converter Slag	3.24	0.77	0.17	Tr.	51.4	19.0	0.87
CSb	(Slow-cooled Samples)	2.87	0.78	0.17	Tr.	50.7	21.2	0.70
FFS	Flash Furnace Slag (Slow-cooled in Ladle)	0.45	0.23	0.42	0.09	40.9	34.6	0.94
EFSa	Electric Furnace Slag (Water-granulated)	0.22	0.13	0.28	0.10	34.3	35.7	0.54
EFSb	Electric Furnace Slag (Ladle Dump Slag)	0.32	0.09	0.21	0.06	37.4	34.1	n.a.
BFSa	Blast Furnace Slag	0.17	0.06	0.15	0.05	31.8	34.3	1.01
BFSb	(Ladle Dump Slag)	0.28	0.15	0.17	0.06	38.5	29.3	1.87
MFSa	Mitsubishi Furnace Slag	0.04	0.09	0.85	3.77	42.0	34.2	0.59
MFSb	(Water-granulated)	0.05	0.10	0.71	3.30	38.6	33.7	0.49

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The Pressure Leaching Conditions are given in Table 2. In all cases the slags were crushed and finely ground, in similar manner, to a particle size largely minus 100 mesh, before being subjected to pressure leaching. The Extraction Results are summarized in Table 3.

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EXAMPLE 1

Two pressure leaching tests, CSa-1 and CSa-2, were carried out on finely-ground samples of slow-cooled, crystallized converter slag samples obtained from a nickel sulphide concentrate smelter. Although the sulphuric acid concentrations and pulp densities were different, the important parameter of leaching temperature was 250°C in both cases; but the significant difference was that in Test CSa-2 an oxygen over-pressure of 75psi was applied, as seen in Table 2.

The results given in Table 3 show the dramatic improvement achieved in Test CSa-2 where the oxygen over-pressure was applied. Accordingly, an oxygen over-pressure was applied in all subsequent tests.

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Table 2: Pressure Leaching Conditions

Leach No.	Reactants				Leach Conditions			
	Slag	H₂O	H₂SO₄	Pulp Density	Temp.	O₂ press.	Total Press.	Time
	g	g	% of Slag	% Solid	°C	+psi	psi	Min
CSa-1	300	700	30	27.5	250	0	577	60
CSa-2	200	800	50	18.0	250	75	652	60
CSb-1	300	700	30	27.5	250	75	652	5-60
FFS-1	300	700	30	27.5	250	75	652	10-90
FFS-2	300	700	15	28.7	250	75	652	10-120
FFS-3	300	700	20	28.3	200	75	300	10-120
FFS-4	300	700	20	28.3	225	75	445	10-120
FFS-5	300	700	20	28.3	250	75	652	10-120
FFS-6	300	700	20	28.3	275	75	940	10-60
EFSa-1	300	700	30	27.5	200	75	300	10-60
EFSa-2	300	700	30	27.5	250	75	652	10-60
EFSb-D	300	700	30	27.5	250	75	652	5-60
EFSa-G-SC	300	700	30	27.5	250	75	652	5-60
EFSb-D-FC	300	700	30	27.5	250	75	652	5-60
BFSa-1	300	700	30	27.5	200	75	300	10-60
BFSa-2	300	700	30	27.5	250	75	652	10-60
BFSb	300	700	30	27.5	260	75	755	5-60
MFSa	300	700	30	27.5	250	75	652	5-60
MFSa-SC	270	630	30	27.5	250	75	652	5-60
MFSb	300	700	40	26.7	250	75	652	30-120
MFSb-SC	300	700	40	26.7	250	75	652	30-120

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Table 3: Extraction Results

Leach No.	RXN Time	Solution (g/L)						%Extraction					
	Min	Ni	Co	Cu	Zn	Fe	Si	Ni	Co	Cu	Zn	Fe	Si
CSa-1	60	2.70	1.25	0.00	0.01	0.60	0.44	18.6	36.3	0.0	19.9	0.3	1.1
CSa-2	60	8.51	2.33	0.56	0.05	1.43	0.45	93.7	93.1	91.3	100	1.1	2.0
CSb-1	30	16.8	4.36	0.75	n.a.	0.77	0.61	91.5	89.4	88.0	n.a.	7.4	10.5
	60	18.1	4.78	0.82	n.a.	0.66	0.59	97.3	96.9	94.8	100	6.2	10.0
FFS-1	60	2.61	1.20	1.93	0.46	0.61	0.55	94.3	95.2	90.6	86.0	0.3	0.6
	90	2.67	1.22	1.94	0.45	0.72	0.55	96.0	96.5	90.6	85.3	0.3	0.6
FFS-2	60	2.09	1.09	1.98	0.42	0.05	0.59	86.0	93.6	89.2	83.6	0.0	0.7
	90	2.19	1.11	1.99	0.43	0.02	0.59	90.4	95.3	90.0	85.6	0.0	0.7
	120	2.23	1.11	1.96	0.43	0.01	0.58	91.9	96.0	90.0	86.4	0.0	0.7
FFS-3	60	1.49	0.77	1.43	0.36	1.36	0.50	71.1	82.7	85.7	70.4	0.8	0.7
	90	1.57	0.81	1.42	0.35	1.10	0.46	74.9	86.5	84.9	69.8	0.6	0.7
	120	1.64	0.82	1.42	0.39	0.91	0.44	78.1	88.0	84.8	77.4	0.5	0.6
FFS-4	60	1.92	0.99	1.87	0.44	0.53	0.51	80.6	88.3	84.5	82.2	0.3	0.7
	90	2.06	1.01	1.91	0.43	0.44	0.49	86.3	90.4	85.9	81.5	0.2	0.6
	120	2.23	1.08	2.02	0.46	0.46	0.47	93.4	96.3	90.7	86.4	0.2	0.6
FFS-5	60	2.19	1.08	2.03	0.46	0.27	0.56	85.6	87.7	85.4	82.1	0.1	0.7
	90	2.25	1.09	2.03	0.45	0.25	0.55	87.9	88.7	85.5	81.1	0.1	0.7
	120	2.48	1.21	2.23	0.49	0.32	0.53	96.2	97.4	93.4	87.6	0.2	0.6
FFS-6	30	2.23	1.07	2.02	0.42	0.22	0.64	92.6	94.2	89.9	85.0	0.1	0.8
	60	2.33	1.11	2.09	0.43	0.21	0.62	96.4	97.3	93.1	87.0	0.1	0.8

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Table 3 (Cont.): Extraction Results (Continue from previous page)

Leach No.	RXN Time	Solution (g/L)						%Extraction					
	Min	Ni	Co	Cu	Zn	Fe	Si	Ni	Co	Cu	Zn	Fe	Si
EFSa-1	30	0.30	0.18	0.39	0.14	3.90	0.34	23.0	46.8	44.1	37.4	2.8	0.5
	60	0.34	0.20	0.44	0.16	2.79	0.33	25.9	52.0	49.3	42.9	2.0	0.5
EFSa-2	30	0.26	0.15	0.30	0.10	0.39	0.43	26.0	32.4	33.8	19.2	0.3	0.7
	60	0.27	0.16	0.32	0.11	0.36	0.42	27.9	35.0	36.6	21.6	0.3	0.6
EFSb-D	30	1.09	n.a.	0.66	n.a.	n.a.	0.60	90.0	n.a.	76.6	n.a.	n.a.	2.5
	60	1.03	n.a.	0.64	n.a.	n.a.	0.60	85.1	84.1	74.3	68.8	n.a.	2.5
EFSa-G-SC	60	0.58	0.05	0.55	n.a.	3.11	n.a.	87.0	81.2	72.8	59.3	3.4	n.a.
EFSb-D-FC	30	0.25	n.a.	0.03	n.a.	1.09	0.63	16.2	n.a.	7.76	n.a.	26.3	4.1
	60	0.35	n.a.	0.11	n.a.	0.55	0.62	22.9	23.0	29.0	23.7	13.5	4.1
BFSa-1	30	0.72	0.21	0.58	0.16	4.08	0.36	89.4	84.4	93.4	61.7	3.0	0.5
	60	0.74	0.22	0.56	0.17	1.82	0.35	94.7	89.9	92.4	68.9	1.4	0.5
BFSa-2	30	0.76	0.22	0.58	0.16	0.41	0.45	91.3	85.4	87.2	62.9	0.3	0.7
	60	0.81	0.24	0.61	0.18	0.47	0.44	96.8	92.8	92.5	71.8	0.4	0.7
BFSb	30	1.44	0.52	0.77	n.a.	0.28	0.62	93.5	91.6	93.3	n.a.	9.4	12.7
	60	1.47	0.55	0.78	0.01	0.36	0.62	94.4	95.2	93.6	89.3	11.8	12.4
MFSa	30	0.07	0.07	2.52	10.9	0.67	0.64	48.8	39.0	52.9	53.8	6.7	3.8
	60	0.08	0.10	2.76	11.8	0.84	0.62	56.8	57.6	57.4	58.2	8.3	3.6
MFSa-SC	30	0.01	n.a.	1.54	6.12	0.14	0.70	11.6	n.a.	58.5	50.3	7.2	8.7
	60	0.05	0.03	2.02	9.07	0.28	0.64	65.9	72.7	75.6	73.4	14.1	7.9
MFSb	60	0.11	0.23	2.00	8.8	0.68	n.a.	38.3	37.3	33.0	38.3	0.0	n.a.
	90	0.12	0.25	2.17	9.5	0.73	n.a.	42.8	40.9	35.3	42.4	0.0	n.a.
	120	0.13	0.27	2.30	10.3	0.73	n.a.	46.0	43.7	37.3	45.2	0.0	n.a.
MFSb-SC	60	0.22	0.37	3.40	15.7	1.68	n.a.	79.9	78.1	80.4	70.7	0.0	n.a.
	90	0.22	0.47	3.48	16.1	1.69	n.a.	80.0	79.5	81.8	71.9	0.0	n.a.
	120	0.25	0.53	3.88	18.1	1.95	n.a.	92.8	90.4	92.7	82.0	0.0	n.a.

A second slow-cooled converter slag sample of slightly different composition, Test CSb-1, was treated under similar conditions to Test CSa-2, except the pulp density was higher and the acid addition lower. Very high degrees of extraction of nickel, cobalt, copper and zinc were achieved,

demonstrating the reproducibility of high extractions and the efficacy of the present invention.

EXAMPLE 2

5   An extensive series of pressure leaching tests were carried out on finely-ground slow-cooled furnace slag samples from oxygen flash smelting of nickel-copper sulphide concentrates. In commercial practice, this particular furnace slag is skimmed into large ladles, which are hauled to and emptied at a slag dump. During the periods of skimming and transporting to the dump, the fayalite

10   slag begins to slowly solidify and crystallize, and is partially solidified at the time of dumping. The samples tested, herein, were representative of a ladle-full of such furnace slag that had been slowly and completely solidified in the ladle itself As seen in Table 2, (note the FFS series), various acid additions and leaching temperatures were tested; and in several of the tests the settling and filtration

15   properties of the leached residues were studied.

Referring to the results shown in Table 3, leaching at the low temperature of 200°C (Test FFS-3), yielded only 78% of the nickel even after 120 minutes of leaching. Leaching at 225°C and the same sulphuric acid addition of 20% by weight of the slag (Test FFS-4), yielded some 80% of the nickel in 60 minutes,

20   some 86% in 90 minutes and some 93% in 120 minutes. Even with addition of only 15% by weight of acid but at 250°C (Test FFS-2), some 86% of the nickel was extracted in 60 minutes and some 92% in 120 minutes. However, addition of 30% by weight of acid and a leaching temperature of 250°C (Test FFS-1)

yielded the best extraction results of some 94% of the nickel in 60 minutes and some 96% in 90 minutes. Test FFS-6 at 275°C yielded some 96% of the nickel in 60 minutes, slightly better than in Test FFS-1 at 250°C; however in commercial practice, the substantially higher total pressure of 940 psi would necessitate a much more robust autoclave.

Of practical interest, were the comparative settling rates of leached residues from Tests FFS-4, Test FFS-5 and Test FFS-6 carried out under similar leaching conditions except for different leaching temperatures, and a shorter reaction time of only 60 minutes for Test FFS-6, see Table 4. Measurements were taken after 180 minutes of settling. Referring to Table 4, The leaching temperature of 250°C, falling between 225°C and 275°C, yielded a leached residue with the better settling properties, which is an advantage in commercial practice.

Table 4

Test Number	Leach Temp.°C	Leach time min.	Settled Vol. % of original	Calculated % Solids In pulp
FFS-4	225	120	63.4	38.3
FFS-5	250	120	56.0	42.7
FFS-6	275	60	59.0	41.4

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EXAMPLE 3

A third series of pressure acid leaching tests were carried out on finely-ground slags emanating from an electric copper-nickel smelting furnace. In current practice, the hot furnace slag, usually at a temperature above about 1200°C, is quenched directly in excess water, i.e. extremely rapidly solidified and cooled, with the result that crystallization is inhibited and amorphous slag granules are produced (slag sample EFSa). In past practice the furnace slag was skimmed into large slag ladles and transported by rail to a slag dump for disposal (slag sample EFSb).

As seen in Table 3, Test EFSa-1 and EFSa-2, at leaching temperatures of 200°C and 250°C respectively, with all other conditions being similar, yielded surprisingly low extractions of all three metals, nickel, cobalt and copper. Less than 30% of the nickel, less than 50% of the copper and at best some 50% of the cobalt were extracted in 60 minutes of leaching. This surprising discovery led to in-depth investigation of the impact of the physical nature of furnace slag on its susceptibility to acid pressure leaching for extraction of its metal values.

A sample of electric furnace dump slag from previous operations of the same electric furnace before conversion to slag granulation was subsequently subjected to similar leaching conditions. This dump slag had been skimmed into large ladles and hauled by train to a slag dump, allowing for a good measure of slow cooling and crystallization before being dumped. As seen in Table 3, Test EFSb-D at a leaching temperature of 250°C yielded a nickel extraction of some 85% in 60 minutes, dramatically better than the results obtained with the

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amorphous granulated slag. This discovery led to the conclusion that the initial cooling of furnace slags should be sufficiently slow to induce and promote the formation and crystallization of fayalite. Further experiments were carried out to confirm this conclusion.

5   A sample of the electric furnace dump slag was re-melted in the laboratory and rapidly quenched by pouring the hot molten slag at a temperature of about 1200°C directly into a bucket of water. The cooled granules were finely ground and subjected to acid pressure leaching at a temperature of 250°C. As seen in Table 3, Test EFSb-D-FC yielded extractions of nickel, cobalt and copper under

10   30%. The dramatic advantage of a crystallized slag over an amorphous slag was confirmed. However, one more pertinent test was conducted to demonstrate, unequivocally, that amorphous fayalite slags yield poor extractions of their base metal values when subjected to acid pressure leaching, as compared to slags that are initially cooled sufficiently slowly to induce a good measure of

15   crystallization.

        The electric furnace granulated slag was re-melted in the laboratory and initially cooled slowly through the temperature range between about 1200°C and about 1000°C at about 2°-3°C per minute. The cooled slag was finely ground and subjected to acid pressure leaching at 250°C. As seen in Table 3, Test

20   EFSa-G-SC yielded a nickel extraction of 87% in 60 minutes, a cobalt extraction of about 80% and a copper extraction of about 73%. Leaching for a longer period of time, of say 90 minutes, would undoubtedly have yielded higher degrees of extractions.

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The fact that the slags that yielded the poor extractions had an amorphous structure is evident from the X Ray Diffraction patterns shown in Figure 6, which can be compared with the X Ray Diffraction patterns of slags that yielded high levels of extractions shown in Figure 7.

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EXAMPLE 4

In another group of tests, dump slags from a retired nickel-copper blast furnace operation were sampled, crushed, finely-ground and subjected to acid pressure leaching (note the BFS series). These slags had been skimmed into

10   large ladles and transported by train to the slag dumps. The total time of skimming and transporting would generally not be less than 20 minutes and not more than about 60 minutes, giving sufficient time for a good measure of initial slow cooling and crystallization to take place before dumping, with completion of solidification and final cooling on the dump itself. Samples were obtained from

15   two different dump locations, with one sample containing substantially more nickel, cobalt and copper values than the other.

As seen from Table 3, Test BFSa yielded good extractions of the nickel, cobalt and copper even at a leaching temperature of 200°C, although 250°C yielded a nickel extraction of nearly 97% in 60 minutes. The higher-grade

20   slag,Test BFSb, also yielded extractions of some 94% or better.

An important feature of the present invention is that initial slow cooling to induce and effect a good measure of crystallization is necessary in order to

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render fayalite slags amenable to yielding high extractions of their metal values by acid pressure leaching; and that the time that it normally takes to skim a furnace slag and transport it to a dump for disposal and final solidification and cooling, is sufficiently long to effect the necessary degree of crystallization.

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EXAMPLE 5

In this example, (note the MFS series) samples of regular, as-received granulated fayalite slag from a modern Mitsubishi continuous copper smelting operation, containing significant quantities of zinc, lesser amounts of copper and

10   minor quantities of nickel and cobalt, were finely-ground and subjected to leaching conditions similar to those used on the slags from nickel-copper smelting operations.

In Test MFSb the sample was subjected to higher acid addition and longer leaching times than the sample in Test MFSa, as can be seen from Table 2. In

15   both tests, all of the extractions were low, and the highest zinc extraction was 58.2%.

The samples were then re-melted and then slow cooled through the initial solidification temperature range of about 1250°C to about 1000°C. The sample for Test MFSaSC was cooled through the range 1150°C to 1050°C at about

20   3°C/min., and permitted to further cool slowly in the crucible to complete solidification. The sample for Test MFSbSC was cooled through the range 1175° to 1025° at rates that varied between 7°C/min. and 3°C/min, a slowing down due

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to the heat of fusion. As seen from Table 3, the slow cooled samples, which had been given time to crystallize yielded vastly superior extractions.

The pregnant solutions obtained from Test MFSb and Test MFSbSC, which included the wash waters along with the leachates after separation of the solid residues, were combined and were carried through metal recovery stages to render an intermediate product containing the bulk of the metal values that had been extracted from the furnace slags. The first treatment was partial neutralization with limestone to a pH of 4, to precipitate the bulk of the iron. After solid-liquid separation, the liquid was reacted with sodium sulphide to precipitate its contained base metals. The final sulphide precipitate, i.e., the intermediate product, analyzed: 36.6% Zn, 8.35% Fe, 3.75% Cu, 1.00% Co, 0.45% Ni and .0.07% Mn. Recoveries of zinc and cobalt from the pregnant solution were just over 90%, recovery of nickel was 88%, but the recovery of copper was only 41%. Over 80% of the manganese reported in the final barren solution, and only 12% reported in the sulphide product.

Those skilled in the art will recognize that gaseous H_2S or other sulphide compound such as NaHS could be employed to effectively precipitate the base metals from the pregnant solution and they will also be aware of several neutralizing agents that can precipitate hydroxide or carbonate intermediate products.

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The foregoing description of the preferred embodiments of the invention has been presented to illustrate the principles of the invention and not to limit the invention to the particular embodiment illustrated. It is intended that the scope of the invention be defined by all of the embodiments encompassed within the

5   following claims and their equivalents.

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THEREFORE WHAT IS CLAIMED IS:

1. A process of extracting metal values from base metal metallurgical fayalite slags, comprising the steps of:

cooling molten fayalite slag at a sufficiently slow solidification rate for producing a substantially crystallized fayalite slag and to avoid obtaining a substantially amorphous fayalite slag;

crushing and grinding said crystallized fayalite slag and pulping said ground crystallized fayalite slag with water to produce a pulped slag;

adding an effective amount of sulphuric acid to the pulped slag to produce a mixture of sulphuric acid and pulped slag, agitating said mixture at elevated temperatures above about 200°C and elevated pressures, under an over-pressure of oxygen for an effective period of time whereby metal oxides are leached from said pulped ore to produce a leach pulp;

separating the leach pulp into a leachate and leached tailings; and

recovering metal values from said leach pulp.

2. The process according to claim 1 wherein prior to said step of separating the leach pulp into a leachate and leached tailings, said leach pulp is mixed with limestone to raise a pH of the leach pulp to a value between about 3.5 to about 4.5 to precipitate dissolved iron present in said leach pulp.

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3.   The process according to claims 1 or 2 wherein said metal values include any of nickel, copper, cobalt and zinc.

4. The process according to claims 1, 2 or 3 wherein said elevated temperatures are between about 200°C and 275°C and said oxygen over-pressures are between about 15 and 75 psi for total pressures between about 300 psi and about 940 psi, and with the sulphuric acid addition being in excess of stoichiometric requirements after taking into account the acid generated by oxidation of the sulphide sulphur contained in said slags.

5.   The process according to claims 1, 2, 3 or 4 wherein the sulphuric acid employed for digestion of the slag is present in an amount of between about 15% and 40% by weight of the slag, and wherein the pulped slag has a pulp density between about 20% and 30% solids.

6.   The process according to claims 1, 2, 3, 4 or 5 wherein the sulphuric acid employed for digestion is present in an amount of about 30% by weight of the slag, and the reaction temperature is about 250°C.

7.   The process according to claims 1, 2, 3, 4, 5 or 6 wherein the base metal metallurgical fayalite slag is a smelter waste slag.

8. The process according to claim 7 wherein said smelter waste slag is produced by smelting of copper and nickel sulphide ores and concentrates.

9. The process according to claim 7 wherein said waste smelter slag is produced by smelting of copper sulphide ores and or concentrates containing zinc, and/or nickel, and/or cobalt as minor constituents.

10. The process according to claims 1, 2, 3, 4, 5 or 6 wherein the base metal metallurgical fayalite slag is an intermediate converter slag.

11. The process according to claim 10 wherein the intermediate converter slag is produced by smelting of copper and nickel sulphide ores and concentrates.

12. The process according to claims 1, 2, 3, 4, 5, 6, 7, 8, 9, 10 or 11 wherein said solidification rate to effect crystallization through a temperature range between about 1200°C and about 1050°C is between about 1°C/minute and about 10°C/minute.

13. The process according to claims 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11 or 12 wherein hot, molten iron silicate slag at a smelting temperature of about 1150°C to about 1300°C is skimmed into slag ladles, in which ladles initial cooling begins by heat radiation from said ladles and in which further cooling continues during

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holding and transport to a slag dump, over a total time period of at least about 15

minutes and up to about 60 minutes, before being discharged onto a slag dump

for final solidification and cooling.

14. The process according to claims 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12 or 13

wherein said sulphuric acid is produced as a by-product of smelting of copper

and nickel sulphide ores and concentrates, used to produce said metallurgical

slags.

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Energy Sources
Coke
Coal
Natural Gas
Electricity
Oxygen

Feed Sources
Lumpy Ores
Concentrates
 Dried
 Calcined········▸
 Sintered ···········▸

| SO2 goes to Recovery or to Stack |

Siliceous ────▸
Flux

PRIMARY SMELTING STAGE

Blast Furnace ------------------------------▸
Reverberatory Furnace-----------------------▸
Electric Furnace _____▸
Oxygen Flash Smelting Furnace----------
Mitsubishi Continuous Smelting ------------▸

| Gases to Stack |

| SO2 goes to Recovery |

Molten
Furnace
Matte

Molten
Converter
Slag

Siliceous ────▸
Flux

CONVERTING

········▸ | SO2 goes to Recovery or to Stack |

Waste Furnace Slags

To Dumps by way of
Slag ladles and Trains or
To Dumps by way of
Granulation and pumping

Intermediate Products

Nickel-Copper Matte or
Blister Copper

PRIOR ART

Conventional Nickel-Copper Smelting

FIGURE 1

● ●

**NICKEL-COPPER-COBALT SULPHIDE
FEEDS AND FLUXES**

PRIMARY SMELTING FURNACE

WASTE/DUMP SLAG

CONVERTER SLAG

NICKEL-COPPER-COBALT
FURNACE MATTE

CONVERTING

COOLING/CRYSTALLIZATION

NICKEL-COPPER-COBALT
BESSEMER MATTE

CRUSHING & GRINDING

WATER

PULPING

BY-PRODUCT

SULPHURIC
ACID

PRESSURE LEACHING

OXYGEN

WATER

FLOCCULANT

COUNTER-CURRENT-DECANTATION

TO TAILINGS PLACEMENT

NEUTRALIZING &

PRECIPITATION
AGENTS

METALS RECOVERY

TO WASTE WATER
TREATMENT
& DISPOSAL

**INTERMEDIATE
NICKEL-COPPER-COBALT PRODUCTS**

FIGURE 2

LEGEND
Solids ⟶
Pulps ----→
Liquids ••••••►
Gases ·········►

NICKEL-COPPER-COBALT SULPHIDE FEEDS AND FLUXES

↓

PRIMARY SMELTING FURNACE

WASTE/DUMP SLAG   CONVERTER SLAG

NICKEL-COPPER-COBALT FURNACE MATTE

↓

CONVERTING

↓

NICKEL-COPPER-COBALT BESSEMER MATTE

COOLING/CRYSTALLIZATION

↓

CRUSHING & GRINDING

↓

WATER → **PULPING**

↓

BY-PRODUCT → **PRESSURE LEACHING** ← OXYGEN
SULPHURIC ACID

↓

LIMESTONE → **PARTIAL NEUTRALIZATION/ IRON PRECIPITATION**

↓

FLOCCULANT → **COUNTER-CURRENT-DECANTATION** ----> TO TAILINGS PLACEMENT
WATER →

↓

NEUTRALIZING & → **METALS RECOVERY** ·······> TO WASTE WATER
PRECIPITATION   TREATMENT
AGENTS   & DISPOSAL

↓

INTERMEDIATE NICKEL-COPPER-COBALT PRODUCTS

LEGEND	
Solids	——————→
Pulps	– – – – →
Liquids	·······>
Gases	············>

FIGURE 3

● ●

NICKEL-COPPER-COBALT SULPHIDE
FEEDS AND FLUXES

↓

PRIMARY SMELTING FURNACE

WASTE/DUMP SLAG

NICKEL-COPPER-COBALT
FURNACE MATTE

TO DISPOSAL AREA

CONVERTING

COOLING/CRYSTALLIZATION

NICKEL-COPPER-COBALT
BESSEMER MATTE

CRUSHING & GRINDING

WATER ··········▶ **PULPING**

BY-PRODUCT ··········▶
SULPHURIC
ACID

PRESSURE LEACHING ◀·········· OXYGEN

WATER ··········▶
FLOCCULANT ··········▶

COUNTER-CURRENT-DECANTATION ------▶ TO TAILINGS
PLACEMENT

NEUTRALIZING & ------▶
PRECIPITATION
AGENTS

METALS RECOVERY ··········▶ TO WASTE WATER
TREATMENT
& DISPOSAL

↓

**INTERMEDIATE
NICKEL-COPPER-COBALT PRODUCTS**

LEGEND
Solids ———▶
Pulps ------▶
Liquids ··········▶
Gases ·················▶

FIGURE 4

NICKEL-COPPER-COBALT SULPHIDE
FEEDS AND FLUXES

PRIMARY SMELTING FURNACE

WASTE/DUMP SLAG

NICKEL-COPPER-COBALT
FURNACE MATTE

TO DISPOSAL AREA

CONVERTING

COOLING/CRYSTALLIZATION

NICKEL-COPPER-COBALT
BESSEMER MATTE

CRUSHING & GRINDING

WATER

PULPING

BY-PRODUCT

SULPHURIC
ACID

PRESSURE LEACHING

OXYGEN

LIMESTONE

**PARTIAL NEUTRALIZATION/
IRON PRECIPITATION**

FLOCCULANT

WATER

COUNTER-CURRENT-DECANTATION

TO TAILINGS
PLACEMENT

NEUTRALIZING &

PRECIPITATION
AGENTS

METALS RECOVERY

TO WASTE WATER
TREATMENT
& DISPOSAL

INTERMEDIATE
NICKEL-COPPER-COBALT PRODUCTS

LEGEND
Solids
Pulps
Liquids
Gases

FIGURE 5

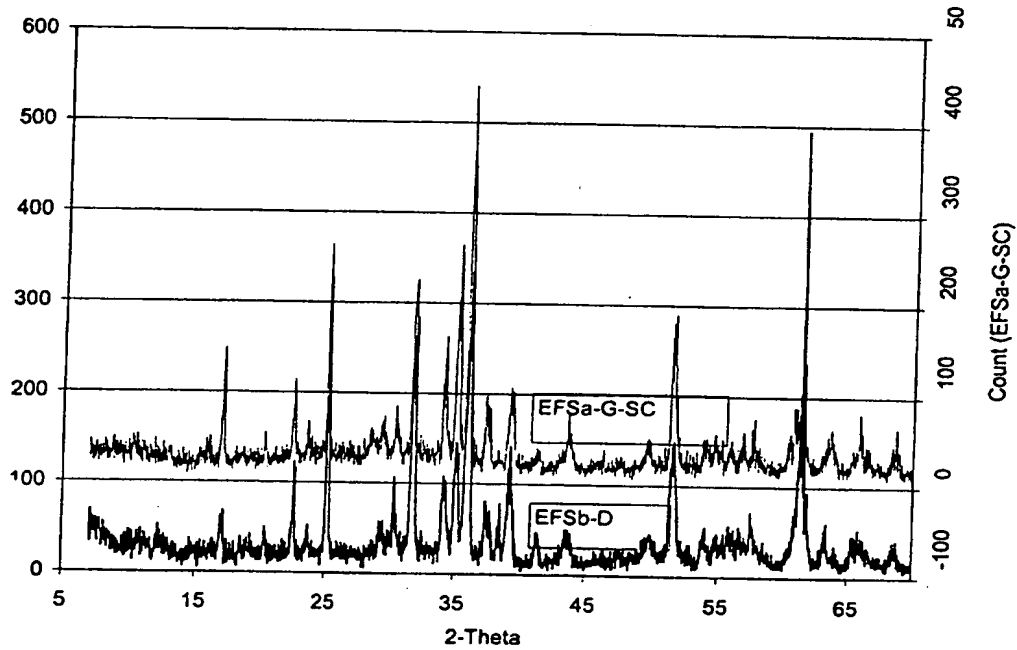Figure 6:XRD of two Electric Furnace Feed slags with poor Ni/Co recovery

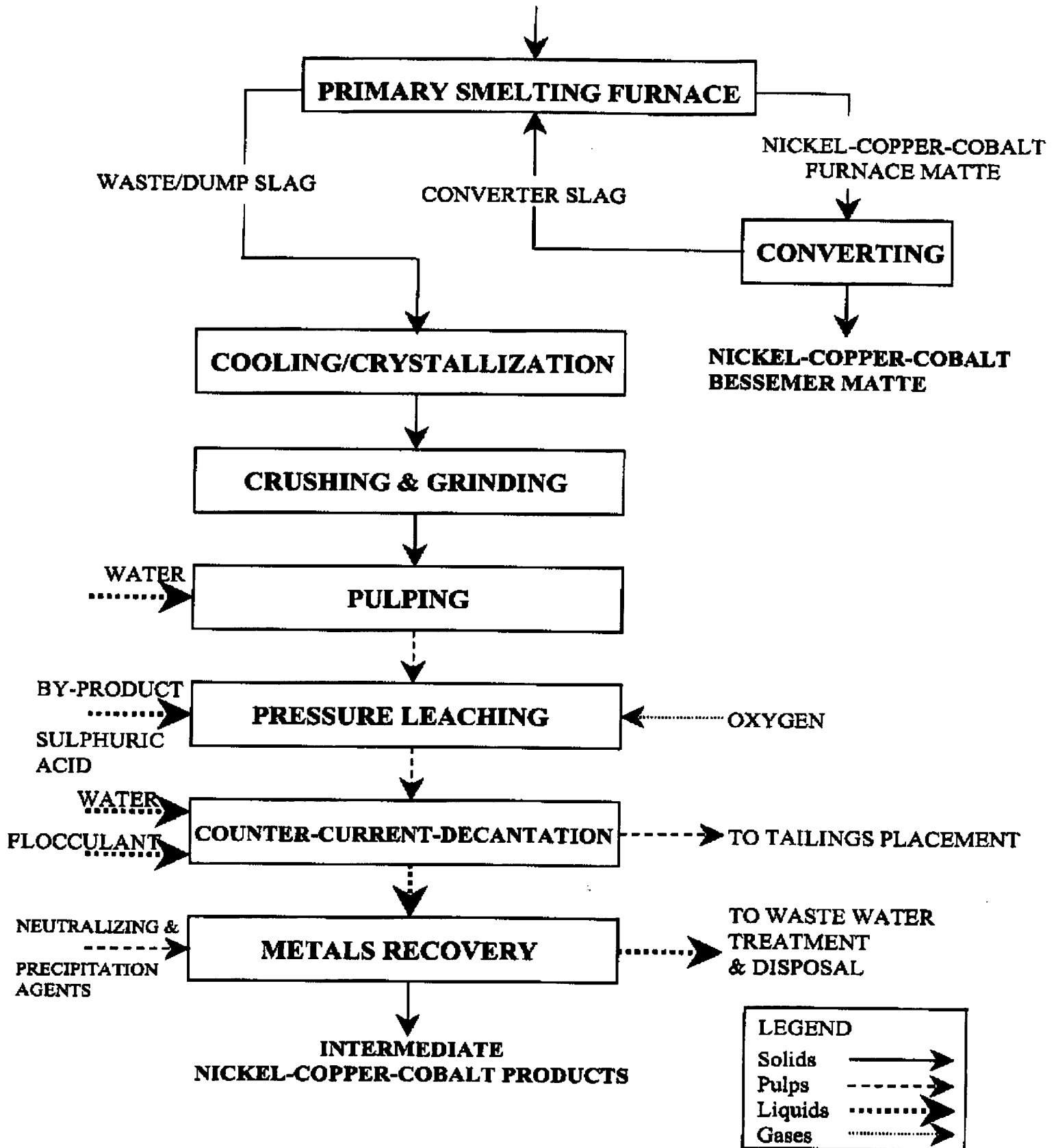Figure 7: XRD of two Electric Furnace Feed slags with good Ni/Co recovery

NICKEL-COPPER-COBALT SULFIDE
FEEDS AND FLUXES

PRIMARY SMELTING FURNACE

WASTE/DUMP SLAG

CONVERTER SLAG

NICKEL-COPPER-COBALT
FURNACE MATTE

CONVERTING

NICKEL-COPPER-COBALT
BESSEMER MATTE

COOLING/CRYSTALLIZATION

CRUSHING & GRINDING

WATER

PULPING

BY-PRODUCT
SULPHURIC
ACID

PRESSURE LEACHING

OXYGEN

WATER

FLOCCULANT

COUNTER-CURRENT-DECANTATION

TO TAILINGS PLACEMENT

NEUTRALIZING &

PRECIPITATION
AGENTS

METALS RECOVERY

TO WASTE WATER
TREATMENT
& DISPOSAL

INTERMEDIATE
NICKEL-COPPER-COBALT PRODUCTS

LEGEND
Solids
Pulps
Liquids
Gases